

## CHARACTERIZATION OF HAZARDOUS AIR POLLUTANTS FROM COAL-FIRED ELECTRIC UTILITIES

Thomas D. Brown and Charles E. Schmidt  
U.S. DOE/Pittsburgh Energy Technology Center  
P.O. Box 10940  
Pittsburgh, PA 15236-0940

Keywords: air toxic emissions, hazardous air pollutants

### ABSTRACT

This paper briefly describes both recent and ongoing studies being conducted to assess the emissions of hazardous and toxic substances from a variety of coal-fired electric utility power generation systems. Recent developments in the analytical methodology required to measure low levels of toxic metals associated with flyash are presented. Also, current and future U.S. Department of Energy plans to augment these assessments are discussed.

### INTRODUCTION

The trace elements associated with the mineral matter in coal and the various compounds formed during coal combustion have the potential to produce air toxic emissions from coal-fired electric utilities. The recently enacted Clean Air Act Amendments (CAAA) contain provisions that will set standards for the allowable emissions of 190 hazardous air pollutants (HAPS). These 190 air toxics can be associated with any number of source categories that emit pollutants to the environment. Many of these HAPS could possibly be emitted from coal-fired electric generating stations. Coal-fired electric utility boilers will be studied by the Environmental Protection Agency (EPA) to determine if regulation is appropriate and necessary.

When coal is combusted, trace elements associated with the mineral matter are released in both solid and vaporized forms. Those trace elements not vaporized during combustion will report to the bottom ash stream or exit the combustor as particulate matter. The trace elements that are vaporized during combustion will exit the combustor as gases, condense either as submicron particles, or on the surface of particulate matter in the flue gas stream. The condensation of trace elements on particles results in an enrichment in concentration of specific elements (1), as shown in Table 1.

During the first phase of a two-phase program, the Canadian Electric Association (2) conducted a study to examine air, water, and ash pathways for trace constituents released to the environment from four Canadian coal-fired generating stations. All the major input and output streams of the utility plant were sampled for up to 45 elements in addition to polycyclic aromatic hydrocarbons. Material balances were made based on the average of several runs. Material balance closures to within 20% were found for 37 elements. Closure was not obtained for fluorine, silicon, phosphorus, cadmium, mercury, and boron. Table 2 summarizes the emission of elements which are on the EPA HAPS list from the Canadian Electric Association study of coal-fired power plants. The second phase

of the program dealt with the environmental dispersion and biological implications of the release.

The Electric Power Research Institute (EPRI) has begun to assess the emissions from power plants under the PISCES (Power Plant Integrated Systems: Chemical Emission Studies) program. The first activity consisted of an exhaustive literature review to obtain as much existing data as possible on the emission of chemical species from power plants (3). This data was organized into a database that contains information on both individual power plants and on the chemical characteristics of various streams within those plants. The PISCES literature study also served to identify gaps in the existing data on power plant emissions. The second major activity within the PISCES program is the Field Chemical Emissions Monitoring project which involves the use of a consistent and comprehensive analytical protocol to evaluate all inputs and outputs of the pollution control subsystems and all the process streams at the utility for HAPS. To date, the EPRI study has gathered analytical information at ten utility sites for 24 of the 190 hazardous pollutants listed in Title III of the CAAA.

Conventional air pollution control subsystems have the potential to remove many of the air toxic emissions from flue gas generated from the combustion of coal. However, there is a lack of precise analytical data on the removal of toxics across environmental control devices, such as electrostatic precipitators, baghouses, and wet limestone scrubbers. The relative concentrations of some of the toxic materials could also be increased as a result of using these technologies, or toxics could be formed when chemicals are added to the flue gas stream to increase particulate collection efficiency. Further, some of the more advanced SO<sub>2</sub> and NO<sub>x</sub> mitigation technologies involve furnace injection of a sorbent and combustion modification, respectively, and could influence the distribution of toxics between the bottom ash and flue gas streams. To date, little information exists on the effects these advanced technologies have on the amounts of toxic substances formed in the combustion zone.

#### CURRENT DOE AIR TOXICS INVESTIGATIONS

The Pittsburgh Energy Technology Center (PETC) of the U.S. Department of Energy (DOE) has two current investigations, initiated before passage of the CAAA, that will determine the air toxic emissions from coal-fired electric utilities. DOE has contracted with Battelle Memorial Institute and Radian Corporation to conduct studies focusing on the potential air toxics, both organic and inorganic, associated with different size fractions of fine particulate matter emitted from power plant stacks. Table 3 indicates the selected analytes to be investigated during these studies. PETC is also developing guidance on the monitoring of HAPS to be incorporated in the Environmental Monitoring Plans for the demonstration projects in the DOE Clean Coal Technology Program.

#### Battelle Memorial Institute

Battelle Memorial Institute and its subcontractor, Keystone/NEA, will correlate the air toxics produced by a laboratory combustor with those from two operating coal-fired electric utility boilers. A characterization of air toxics associated with the surfaces of fine particles and vapor phase constituents of the stack flue gas of the selected coal-fired units will be made. Both the diluted, cooled flyash particles with adsorbed and condensed material on the surfaces and the hot

gas flyash particles will be collected in three size fractions from the stacks. These size fractions are <0.6, 0.6-2.0, and 2.0-0.5 microns.

An innovative source dilution sampler will be utilized to simulate plume cooling and collect the diluted, cooled particles that may have an increased concentration of certain toxic substances. The hot gas samples, particulate and vapor phase, will be collected by EPA Modified Method 5 procedures. The differences in the two samples will provide information on the characteristics of the overall composition of fine particles, particularly materials of air toxic concern.

Laboratory studies can be more useful under certain circumstances than full-scale studies because these studies provide the flexibility to examine emissions from developing pollution control technologies (i.e., furnace and duct sorbent injection, flue gas conditioning, and various combustion configurations). The coals used by the two coal-fired electric utilities will be used in the laboratory combustion studies, which will indicate the efficacy of using a well-controlled laboratory-scale combustor to simulate emissions from a full-scale unit. Additional results from the Battelle laboratory combustion work will include the further development of more advanced sampling methods for collection of flyash and vapor-phase constituents from flue gas. The results will also assist DOE and EPRI in determining which toxic substances to sample in future emissions characterization studies.

#### **Radian Corporation**

Radian Corporation will collect size-fractionated particles from the stack of a full-scale coal-fired utility boiler and characterize the particles for both bulk and surface chemical composition. The sampling will take place over two different time periods ranging from three to four weeks. This will enable the collection of fine particles during a high-load season (winter), a lower-load season (spring), and load swings. Particulate samples will be collected from the stack effluent under both hot-stack and dilution-cooled conditions.

A source dilution sampler will be utilized to simulate the cooling and dilution that the flue gases and particles experience while entering the atmosphere at the stack exit. A relationship will be sought between the chemical materials found and the size of particles. Also, the effects of cooling and dilution upon the surface condensation of volatile species will be evaluated and characterized. In addition, the carbon content of the particulate matter will be determined in an attempt to correlate any organic compounds found on the dilution-sample particulate with the amount of carbon in the flyash.

To date, Radian has evaluated several sample preparation and analysis procedures in order to select two bulk-composition and three surface-leaching techniques to use on the size-fractionated flyash samples collected from both the hot stack gas and the cooled stack gas from the dilution sampler. To accurately evaluate these methods, a coal flyash was selected that is certified by Brammer Standard Company for 29 trace metals ( $\mu\text{g/g}$ ) and 8 major metals (wt.%), and is sieved instead of ground to produce a homogenous sample of ash particles less than 80 microns in size. Metals targeted for analysis and low detection limits were arsenic, barium, beryllium, cadmium, chromium, copper, cobalt, lead, manganese, mercury, molybdenum, nickel, selenium, and vanadium. These metals were chosen because of their known toxic properties, presence on the CAAA's list of hazardous

substances, or suspected occurrence in flue gas streams from coal-fired utility boilers.

Total composition of the flyash particles was determined by neutron activation and glow discharge mass spectrometry (GDMS). Acceptable recoveries, defined as 80-120% of the standard's certified value, were obtained by neutron activation analysis for Ba, Co, Cu, Mn, and V. Chromium and arsenic recoveries were only slightly outside this range at 124 and 127 percent, respectively. The reproducibility was acceptable (less than 20% relative standard deviation, RSD) for all the target elements except Cd, Cu, and Hg. Cadmium, lead, and beryllium were not detected by neutron activation. GDMS analysis provided acceptable recovery (80-120%) for two elements, chromium and copper. Recovery of the remaining elements was biased low and ranged from 16 to 86% recovery. The reproducibility was acceptable (<20% RSD) for all target analytes except molybdenum and cadmium, which were not detected.

The primary focus of the methods evaluation plan was to determine methods that could leach or dissolve metals from the surface of flyash particles. The five leaching agents studied were chosen based on either selectivity for the metals of interest, the method's similarity to chemical or biological processes, or as modifications of an established method. The five methods were 1) a nitric acid digestion technique that indicates the maximum amount of material available from the alumina-silica flyash matrix (EPA Method 3050); 2) an acetic acid leaching solution prepared according to the Toxicity Characteristics Leaching Procedure to a pH of 4.93 to simulate environmental availability; 3) a simulated gastric fluid made from HCl, pepsin, and NaCl buffered to pH 1.2; 4) a simulated lung fluid prepared from phosphate buffered (pH 7.5) saline solution containing bovine serum (albumin) and dextrose; and 5) a chelating agent specific for arsenic and chromium consisting of buffered (pH 4.4) ammonium pyrrolidine-N-dithiocarbamate solution.

For all five methods, 100 mg of the certified flyash was treated. The three analytical techniques used for the analysis of the leachate samples included inductively coupled argon plasma emission spectrophotometry (ICP), graphite furnace atomic absorption spectrophotometry (GFAA), and inductively coupled argon plasma mass spectrometry (ICP-MS). Results of the ICP, GFAA, and ICP-MS analysis of these leachate samples provided a clear indication that the analytical method's sensitivity and precision are very important. ICP-MS provided lower detection limits than ICP or GFAA for all the matrices tested. ICP-MS has the advantage of detecting elements from Be to U (mass 9 to 238) with quantitation levels of 20 ng/mL to 0.1 mg/mL. Detection limits for 14 metals in this evaluation ranged from 0.002 to 0.13 ng/mL. The detection limits are 10 to 100 times lower than ICP or GFAA. By ICP-MS, the RSD for nitric acid digestion samples was <20% for all target elements except Cd (34% RSD), Cu (25% RSD), and Pb (36% RSD). These diluted samples had elemental concentrations less than 3 ng/mL for all target analytes. With respect to the ICP and GFAA analyses, only arsenic (1% RSD), beryllium (7% RSD), chromium (120% RSD), copper (27% RSD), lead (59% RSD), nickel (40% RSD), selenium (1900% RSD), and vanadium (5% RSD) were detected. Similar results were obtained on the other leachate samples, except the simulated lung fluid sample whose increased viscosity presented sample aspiration problems, indicating the superiority of the ICP-MS technique.

The nitric acid digestion, gastric fluid, and acetic acid leach are the three methods chosen based on the performance criteria when analyzed by ICP-MS. ICP-MS

provides lower detection limits and improved precision than previously obtained by conventional ICP or GFAA methods.

#### FUTURE TOXIC EMISSION STUDIES

A collaborative effort has been initiated by the DOE, the Utility Air Regulatory Group (UARG), EPRI, and the EPA to expand the study of hazardous pollutant emissions from utility boilers. This effort will involve measurements at a number of power plants having different boiler designs, NO<sub>x</sub> control methods, particulate control devices, and SO<sub>2</sub> removal systems (wet and dry). From these measurements, the EPA expects to predict the potential air toxic emissions from coal-fired boilers in 1995 and 2000 (after controls are installed to meet the requirements of the acid rain title of the CAAA). Measurements from plants firing bituminous or subbituminous coal will be used to evaluate the entire range of existing power plant configurations and will form the basis for this study.

DOE has issued a solicitation for proposals to assess selected hazardous/toxic pollutants from a number of utilities that utilize different pollution control and process subsystems while burning either bituminous or subbituminous coal. The power plant configurations addressed in this solicitation are given in Table 4. Objective of this solicitation are to determine the removal efficiencies of pollution control subsystems for selected pollutants and the concentrations of pollutants associated with the particulate fraction of the flue gas stream as a function of particle size. A further objective is to determine mass balances for selected pollutants for a variety of different input and output streams of the power plants and subsequently for the entire power plant.

Results from all the DOE studies will provide input to the congressionally mandated study being conducted by the EPA to assess the impacts of the listed HAPS emissions from coal-fired electric utilities, as required in Title III of the CAAA of 1990. In addition, the data will provide a basis for evaluating the potential effects of air toxics regulation on existing pollution control and auxiliary processes being utilized at electric utilities and on the commercialization of technologies demonstrated under the Clean Coal Technology Program.

#### REFERENCES

1. D.G. Coles, R.C. Rahaini, J.M. Ondov, G.L. Fisher, D. Silberman, and B.A. Prentice, "Chemical Studies of Stack Fly Ash from Coal-Fired Power Plant," Environmental Science and Technology, Vol 13, 4, April 1979.
2. J.C. Evans, K.H. Abél, K.B. Olsen, E.A. Lepell, R.W. Sanders, C.L. Wilkerson, and D.J. Hayes, "Characterization of Trace Constituents at Canadian Coal-Fired Plants - Phase I," Contract Number 0016194, Canadian Electrical Association, January, 1985.
3. F.B. Meserole and W. Chow, "Controlling Trace Species in the Utility Industry, paper presented at the conference Managing Hazardous Air Pollutants: State of the Art, Washington, D.C., November 4-6, 1991.

Table 1. Comparison of Elemental Concentrations in Size-Classified Flyash Fractions (Concentrations in  $\mu\text{g/g}$  unless indicated by %)

| Element      | Fraction 1,<br>18.5 $\mu\text{m}$ | Fraction 2,<br>6.0 $\mu\text{m}$ | Fraction 3,<br>3.7 $\mu\text{m}$ | Fraction 4,<br>2.4 $\mu\text{m}$ |
|--------------|-----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Aluminum, %  | 13.8                              | 14.4                             | 13.3                             | 13.9                             |
| Barium, %    | 0.168                             | 0.245                            | 0.31                             | 0.41                             |
| Calcium, %   | 2.1                               | 2.23                             | 2.3                              | 2.36                             |
| Iron, %      | 2.51                              | 3.09                             | 3.04                             | 3.2                              |
| Magnesium, % | 0.47                              | 0.56                             | 0.60                             | 0.63                             |
| Potassium, % | 0.74                              | 0.80                             | 0.82                             | 0.81                             |
| Silicon, %   | 29.6                              | 28.0                             | 27.5                             | 26.8                             |
| Sodium, %    | 1.22                              | 1.75                             | 1.81                             | 1.85                             |
| Sulfur, %    | 0.101                             | 0.304                            | 0.425                            | 0.711                            |
| Titanium, %  | 0.62                              | 0.74                             | 0.73                             | 0.77                             |
| Antimony*    | 2.6                               | 8.3                              | 13.0                             | 20.6                             |
| Arsenic      | 13.7                              | 56.0                             | 87.0                             | 132.0                            |
| Beryllium*   | 6.3                               | 8.5                              | 9.5                              | 10.3                             |
| Cadmium      | 0.4                               | 1.6                              | 2.8                              | 4.6                              |
| Cerium       | 113.0                             | 122.0                            | 123.0                            | 120.0                            |
| Cesium       | 3.2                               | 3.7                              | 3.7                              | 3.7                              |
| Chromium*    | 28.0                              | 53.0                             | 64.0                             | 68.0                             |
| Cobalt*      | 8.9                               | 17.7                             | 20.3                             | 21.8                             |
| Copper       | 56.0                              | 89.0                             | 107.0                            | 137.0                            |
| Dysprosium   | 6.9                               | 8.5                              | 8.1                              | 8.5                              |
| Europium     | 1.0                               | 1.2                              | 1.2                              | 1.3                              |
| Gallium      | 43.0                              | 116.0                            | 140.0                            | 178.0                            |
| Hafnium      | 9.7                               | 10.3                             | 10.5                             | 10.3                             |
| Lanthanum    | 62.0                              | 68.0                             | 67.0                             | 69.0                             |
| Lead*        | 73.0                              | 169.0                            | 226.0                            | 278.0                            |
| Manganese*   | 208.0                             | 231.0                            | 269.0                            | 309.0                            |
| Neodymium    | 45.0                              | 47.0                             | 49.0                             | 52.0                             |
| Nickel*      | 25.0                              | 37.0                             | 43.0                             | 40.0                             |
| Rubidium     | 51.0                              | 56.0                             | 57.0                             | 57.0                             |
| Samarium     | 8.2                               | 9.1                              | 9.2                              | 9.7                              |
| Scandium     | 12.6                              | 15.3                             | 15.8                             | 16.0                             |
| Selenium*    | 19.0                              | 59.0                             | 78.0                             | 198.0                            |
| Strontium    | 410.0                             | 540.0                            | 590.0                            | 700.0                            |
| Tantalum     | 2.06                              | 2.3                              | 2.5                              | 2.7                              |
| Terbium      | 0.90                              | 1.06                             | 1.10                             | 1.13                             |
| Thorium      | 25.8                              | 28.3                             | 29.0                             | 30.0                             |
| Uranium      | 8.8                               | 16.0                             | 22.0                             | 29.0                             |
| Vanadium     | 86.0                              | 178.0                            | 244.0                            | 327.0                            |
| Tungsten     | 3.4                               | 9.0                              | 16.0                             | 24.0                             |
| Ytterbium    | 3.4                               | 4.1                              | 4.0                              | 4.2                              |
| Zinc         | 68.0                              | 189.0                            | 301.0                            | 590.0                            |

NOTE: These data were taken from Reference 1.

\*Denotes element is contained on EPA HAPS list.

\*\*Aerodynamic cut sizes.

Table 2. Flue Gas Trace Element Releases from  
Selected Canadian Coal-Fired Power Plants

| <u>Element</u> | <u>% of Total Element in Coal<br/>Released with the Flue Gas</u> |
|----------------|--|
| Chlorine       | 49 - 99.0  |
| Chromium       | 0.1 - 8.7  |
| Manganese      | 0.1 - 1.0  |
| Cobalt         | 0.09 - 1.5   |
| Arsenic        | 0.74 - 9.3   |
| Selenium       | 3.5 - 73.0   |
| Antimony       | 0.2 - 2.5  |
| Mercury        | 79.0 - 87.0  |
| Lead           | 0.2 - 1.4  |

Table 3. Compounds and Elements for the Battelle  
and Radian Air Toxics Studies

|  |                                  |
|--|----------------------------------|
| Arsenic  | Ammonia                          |
| Barium   | Radionuclides (Ra, Po, U, etc.)  |
| Beryllium                                      | Sulfates                         |
| Cadmium  |                                  |
| Chromium                                       | Benzene                          |
| Chlorine (as Cl <sup>-</sup> )                 | Toluene                          |
| Cobalt   | Formaldehyde                     |
| Copper   | Polycyclic Aromatic Hydrocarbons |
| Cyanide  |                                  |
| Fluorine (as F <sup>-</sup> )                  |                                  |
| Lead   |                                  |
| Manganese                                      |                                  |
| Mercury  |                                  |
| Molybdenum                                     |                                  |
| Nickel   |                                  |
| Phosphorus (as PO <sub>4</sub> <sup>3-</sup> ) |                                  |
| Selenium                                       |                                  |
| Vanadium                                       |                                  |

TABLE 4.

## ELECTRIC UTILITY CONFIGURATIONS

| Configuration | Coal Rank                   | Particulate Control | SO <sub>2</sub> Control | NO <sub>x</sub> Control <sup>1</sup> | Coal Preparation | Cooling Tower (Water) Streams |
|---------------|-----------------------------|---------------------|-------------------------|--------------------------------------|------------------|-------------------------------|
| 1             | Bituminous                  | ESP                 | None                    | None                                 |                  |                               |
| 2             | Bituminous                  | ESP                 | Wet FGD                 | None                                 |                  |                               |
| 3             | Bituminous                  | ESP                 | Wet FGD                 | All                                  | Yes              | Yes                           |
| 4             | Bituminous                  | Baghouse            | None                    | All                                  |                  |                               |
| 5             | Bituminous or Subbituminous | Baghouse            | Wet or Dry FGD          | All                                  |                  |                               |
| 6             | Bituminous or Subbituminous | ESP                 | Dry FGD                 | All                                  |                  |                               |
| 7             | Subbituminous               | Baghouse            | None                    | All                                  |                  |                               |
| 8             | Subbituminous               | ESP                 | Wet FGD                 | All                                  |                  |                               |

<sup>1</sup> All designation includes low NO<sub>x</sub> burners, overfire air, and "other."